A STUDY OF STANDARD CELLS

by

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I wish to thank Dr. H. P. Cady, under whose direction this work was done, for his many helpful suggestions; also George Cady for the construction of glass cells.

In this work experiments have been carried out investigating Standard cells of the types.

1) Cd Amg : $CdCl_2.5/2H_2O$: AgCl : Ag

2) Cd Amg : $CdCl_2NH_4Cl$: AgCl : Ag

3) Cd Amg : $CdCl_2KCl$: AgCl : Ag

4) Zn Amg : $ZnCl_22NH_4Cl.H_2O$: AgCl : Ag

5) Zn Amg : $ZnCl_22KCl.H_2O$: AgCl : Ag

6) Cd Amg : $CdBr_2.4H_2O$: AgBr : Ag

7) Cd Amg : $CdBr_2NH_4Br$: AgBr : Ag

8) Cd Amg : $CdBr_2KBr.H_2O$: AgBr : Ag

9) Zn Amg : $ZnBr_23NH_4Br.H_2O$: AgBr : Ag

10) Zn Amg : $ZnBr_22KBr.2H_2O$: AgBr : Ag

Cells of the first type have been investigated by Taylor (1), Horsch (2), and Goodwin (3). Goodwin also investigated cells of the type six, but only determined the difference of potential between two cells having different concentrations. De La Rue (4) was the first investigator to make use of the (AgCl : Ag) electrode in making cells. Besides those mentioned above Noyes and Ellis (5), Linhart (6), Lewis (7), and Halla (8) have added to the knowledge of the silver chloride electrode finding it to be entirely reproducible, the potential however depending upon the method of preparation. The use of double salts in standard cells has been investigated by Lipscomb and Hulett (9).

The essential conditions for a voltaic cell are that there be sponteanously and simultaneously occurring oxidation and reduction reactions at two separate and distinct points accompanied by a loss of free energy. Besides this a standard cell must have a fairly high and under fixed conditions a constant electromotive force, must be reproducible, permanent, and it is desirable that it have a small temperature coefficient.

For a cell to have a constant and high electromotive force the oxidizing and reducing agent must be fairly strong. The reducing agent must be far enough removed from hydrogen in the voltaic series that it will not liberate hydrogen from the solution. Zinc and cadmium and their liquid amalgams are the only two metals that have so far answered this requirement.

To be reproducable the salts must be well defined chemically and easy to produce in the pure state, being definite in form and composition over a wide range of temperature.

To be permanent or durable the oxidizing and reducing agent must be difficultly but rapidly soluble, so that the cell will completely recover its former electromotive force after being used.

For a small temperature coefficient it is desirable that the concentrations of the ions do not change or if they do they must be compensating.

Preparation of Materials and Their Purification.

Mercury.- All of the mercury used was purified by distilling at least twice in a current of air under reduced pressure, according to Hulett and Minchin (10).

The essential feature of this method the oxidation of any metals that may distill with the mercury by means of a slow current of air, which was admitted through a tube drawn out at one end to a fine capillary extending almost to the bottom of the distilling flask. This tube passes through a tightly fitting cork in the neck of the flask, and the flow of air regulated by means of a pinch clamp and a short piece of rubber tubing, the free end of which is plugged with cotton to filter out the dust.

An ordinary distilling flask was used, which was connected to a glass tube serving as an air condenser, at the lower end was connected a filter flask. The aspirator was connected to the side tube of the filter flask in the usual manner. The flask was wrapped in sheet asbestos and heated over an asbestos pad. After each distillation the apparatus was taken apart and cleaned with nitric acid. The mercury was considered pure when only a small amount of oxide was found with the mercury in the filter flask. These oxides were removed by passing it through a pinhole in a filter paper. Several operations are necessary before it was entirely free from the oxides, it was filtered until no trace of the oxide could be detected on the filter paper.

Apparatus
for
Cadmium Amalgam

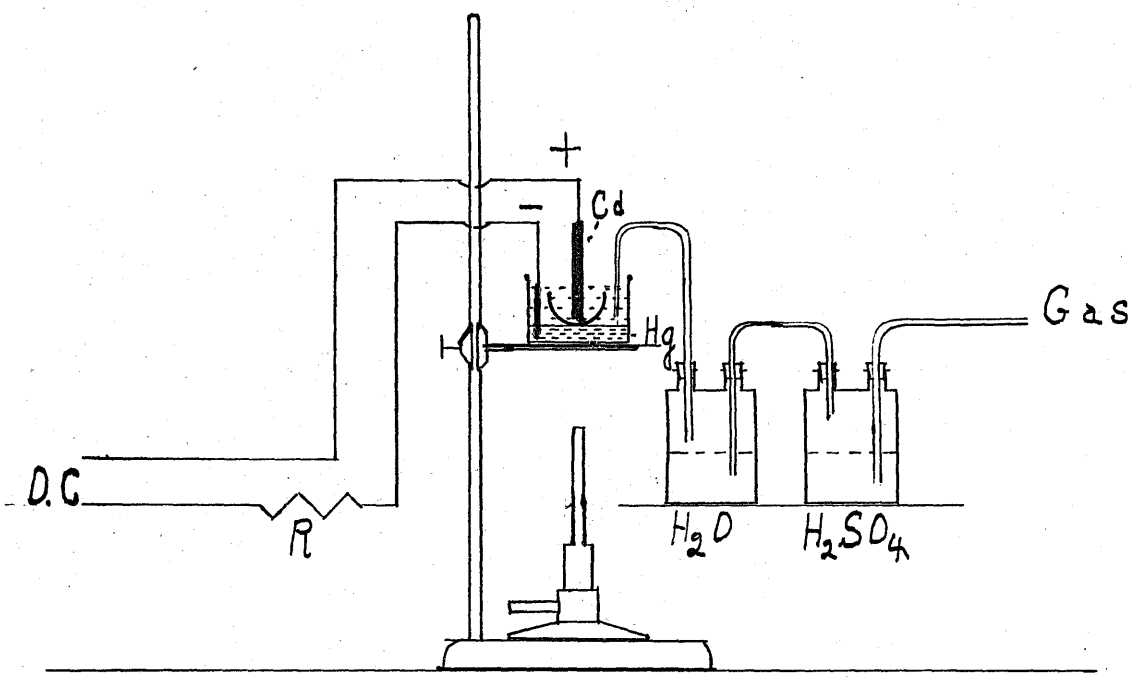


Figure I

Cadmium amalgam.- Cadmium amalgam containing 12.5 percent of cadmium by weight was made electrolytically using a stick of pure cadmium as the anode and pure mercury as the cathode. A little experimenting was necessary before a satisfactory amalgam was prepared, that was free from oxide.

A weighed quantity of pure mercury (Figure I) was placed in a ten centimeter crystallizing dish. A small evaporating dish just large enough to fit nicely in the crystallizing dish was placed on top of the mercury. This served to catch any fragments formed at the anode. The crystallizing dish was filled with a solution of cadmium chloride, made by dissolving crystals of pure cadmium chloride in water. The whole apparatus was placed on a ring about six inches above a burner which was turned as low as possible. This kept the temperature of the solution around seventyfive degrees, which was above the melting point of the amalgam. The solution was stirred by allowing natural gas, which had been washed with sulphuric acid and water, to bubble through. Electrical connection was made to the mercury by means of a platinum wire sealed in the bottom of a glass tube. A current between 0.4 and 0.5 ampere was used, obtained by connecting a 60 watt bulb in series with the 110 direct current. Using 1 farady as 96,500 coulombs, and the molecular weight of cadmium as 112.4 a current of 0.5 ampere will deposit 1.07 grams of cadmium per hour. The current was left on so as to leave an extra amount of cadmium in the amalgam. When the amalgam was weighed additional mercury was added to make a 12.5 percent

amalgam.

Zinc amalgam.- Zinc amalgam was made directly containing 10 percent of zinc. The mercury was heated in a porcelain dish on a sand bath and covered with about a centimeter of parafine to keep the oxide from forming. Pure zinc, previously treated with sulphuric acid to remove the film of oxide, then washed and dried, was placed in the hot mercury. The exposed surfaces of the amalgams were slowly tarnished by oxidation, this was lessened by keeping the amalgams under parafine.

AgCl and Ag Br.- A solution of $AgNO_3$ was treated with HCl and KBr to form the corresponding silver salts. These salts were precipitated and washed until free from nitrates. The salts were then dried in an oven at 100° and kept in a dark place until used. As soon as any effect of the light was noticed fresh salts were prepared.

$CdCl_2$ $2.5H_2O$.- This salt was prepared according to Lipscomb and Hulett (11). A very pure C.P. salt of $CdCl_2$ was brought into solution, H_2S was passed in until a small precipitate was formed. This was allowed to settle for 2 or 3 days and the clear liquid decanted off and set aside in a desiccator to crystallize. If too much water was present the solution was boiled until the solution was almost saturated at 40°. $CdCl_2 2.5H_2O$ is stable between 10° and 40°; at higher temperatures according to Dietz (12) the salt forms another hydrate.

$CdBr_2 4H_2O$.- H_2S was passed into a solution of $CdCl_2$ made form pure C.P. salt with distilled water, until a precipitate

was formed. This displaced any metals from solution having a lower electrolytic potential than cadmium and in addition any metals having sulphides more insoluble than cadmium. The precipitate was allowed to settle, the clear liquid was filtered off and H_2S passed through until precipitation was complete. The precipitate was filtered off and washed with hot H_2O until free from chlorides. This was tested with a silver nitrate solution. The precipitated CdS was transfered to a beaker and covered with distilled water. While the precipitate was mechanically stirred pure bromine was dropped in slowly from a burette. The sulphur is precipitated out and $CdBr_2$ is formed, along with it is also formed $CdSO_4$, which was removed by treating with $BaBr_2$. If an excess of $BaBr_2$ was added a solution of $CdSO_4$ was added until precipitation was complete. This process was repeated until the final solution gave no precipitate with either $CdSO_4$ or $BaBr_2$. The solution was concentrated and set aside to crystallize out. Long needles of $CdBr_2 4H_2O$ were formed, which is the stable phase of $CdBr_2$ at ordinary temperatures.

Bromine.- The bromine used was redistilled from a pure sample of bromine. KBr was added to form KCl with any chlorine present.

$ZnBr_2$.- Pure granulated zinc was treated with bromine. Granulated zinc was covered with distilled water and the bromine dropped in slowly. The reaction is vigorous so the solution was stirred and surrounded with ice water.

$ZnCl_2$, KCl, NH_4, Cl, KBr, NH_4Br.- These salts were obtained in a pure form free from sodium from the storeroom. If sodium was found to be present the salts were recrystallized.

Preparation of Electrodes.

AgCl:Ag electrode.- Pure silver wire 1 milliameter in diameter was drawn out until it had a diameter of 0.381 mm. and cut up into 15 cm. lengths; five cm. was wound into a helix having a diameter of 1.76 mm. and length of 4.14 mm. This helix was wound around a piece of enunciator wire having a diameter of 0.99 mm., the same piece of wire was used throughout.

A bulb was made from thin walled glass tubing 1 cm. long and an inside diameter of 2.18 mm. This was filled with powdered AgCl and heated until the latter was melted when the silver helix was introduced and worked up and down until the helix was completely covered with AgCl. The bulb was withdrawn from the fire and placed in a beaker of water which broke the glass away from the AgCl. The AgCl was trimmed to the length of the helix with a razor blade. Later electrodes were made by dipping the silver helix in molten AgCl which formed a more adherent layer of AgCl around the helix. The AgCl cylinder was slightly larger than the electrode previously discussed and varied in diameter although efforts were taken to make them of the same diameter. They varied from 3 to 3.5 mm. in diameter but caused no difference in electromotive force. The electrodes were sealed in a glass tube of small bore 6 cm. long and drawn to a point just large enough to admit the silver wire. Powdered sealing wax was tapped in from the open end and the tube gently heated until the wax was melted. The tube was next fitted with a cork, notched to allow free passage of air

when placed in the cell. Above the cork was wound one turn of copper enunciator wire, to which the silver wire was soldered. The electrode was completed by running it alternately as anode and cathode in a 10% solution of HCl. It was first run as cathode until a smooth layer of silver was formed around the bulb on the outside, the current was reversed until an even layer of AgCl was formed. If an even layer was not formed it was run again as cathode for 15 seconds and then as anode until a layer of AgCl formed, this operation was repeated until a perfectly smooth and even layer of AgCl was formed. For the finish the electrode was run as cathode for 15 seconds and then as anode for 5 seconds, leaving the electrode black or reddish brown. Each electrode was treated separately and gave cells that were reproducible. A current of between 0.25 and 0.3 was used, obtained by connecting two 60 watt bulbs in series with the 110 D.C. After the electrodes were completed they were soaked in distilled water for 3 or 4 hours, the water being changed every half hour, to free them from any HCl.

AgBr:Ag electrode.- These were first prepared as the silver chloride electrodes were but were not reproducible for various reasons. In the first place the silver bromide stuck to the glass and when the tube was broken away the salt would adhere to it instead of to the silver helix. Here the method of dipping the electrodes was developed, giving satisfactory coatings. In the electrolytic process the electrodes were first run in a 10% solution of KBr, which gave fairly smooth layer of AgBr, but the electrodes were not reproducible. The reproducability of the electrodes was determined on a set of 12 electrodes prepared in a KBr solution. The electrodes were placed in a fresh 10% solution of KBr, one was selected as a reference electrode and the difference of potential between it and each of the others was measured by the potentiometer method. The differences ranged from plus to minus 0.0015 volt giving a difference of 0.003 between the two extremes. A solution of pure HBr was obtained by distillation of a commerical sample, and the electrodes run the same way in it, this still gave unsatisfactory electrodes. It was found by experiment that if the electrodes were reduced instead of oxidized at the finish much more reproducible electrodes could be set up. A new set of electrodes were prepared, they were run alternately in a solution of 10% HBr as anode and cathode as described in the preparation of the silver electrodes, until a smooth even layer of AgBr was formed, then they were run as cathode for 20 seconds,

leaving the electrode black. The greatest deviation from the reference electrode was 0.0002 and the least nothing; the majority differed by only 0.00005 volt. The same current was used as with the silver chloride electrodes. The electrodes were also washed in the same manner.

Standard Cell

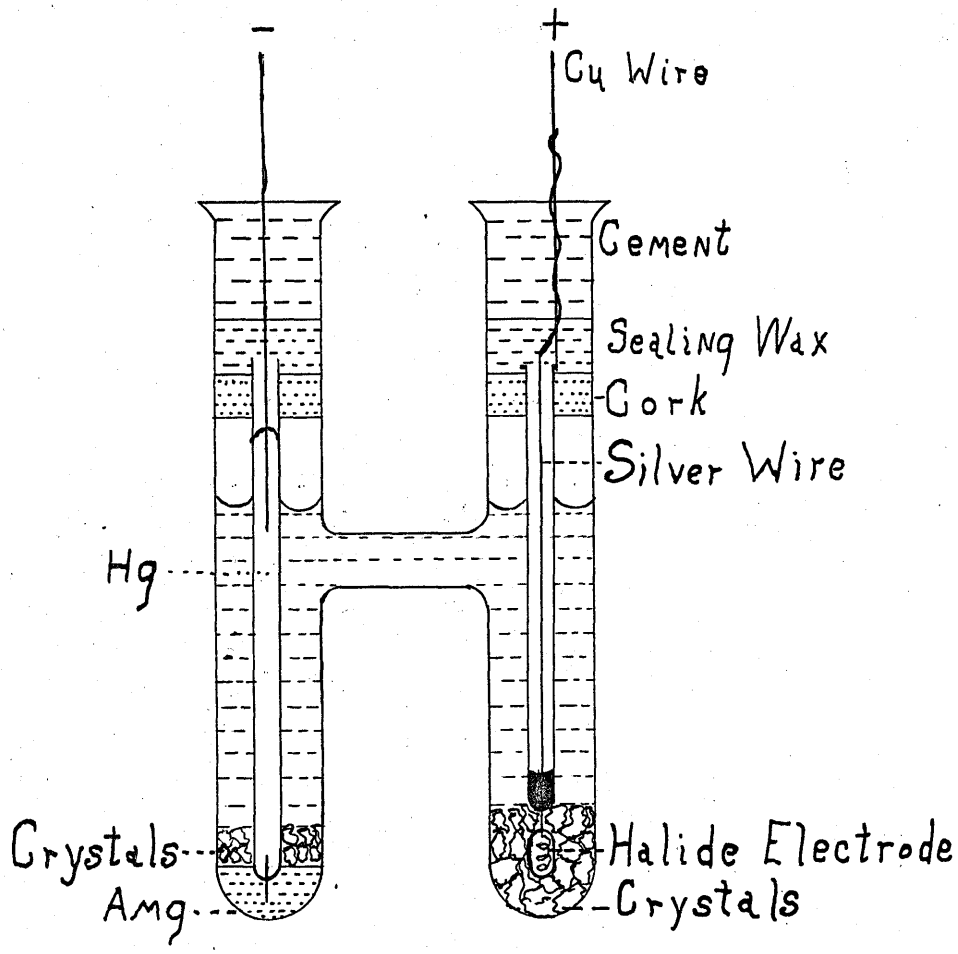


Figure II

The Cells and the Introduction of the Materials.

For facility in filling and sealing the H type of cells was used. Figure II shows the cell set up completely. Connection was made to amalgam by means of a platinum wire sealed in a glass tube; connection to the outside was made by an amalgamated copper wire placed in the mercury that is in the glass tube. The cells were at first only sealed with a cork then with cork and sealing wax but the sealing wax was soluble in the kerosene in which the cells were placed, so a cement of litharge and glycerine was used to seal them; a layer of at least 10 mm. was necessary before sealing was complete. For final sealing and protection from the light the cells were dipped in Acme brand black auto enamel, which when perfectly dry was insoluble in the kerosene. This required that the cells set at least 3 days before placing in temperature baths.

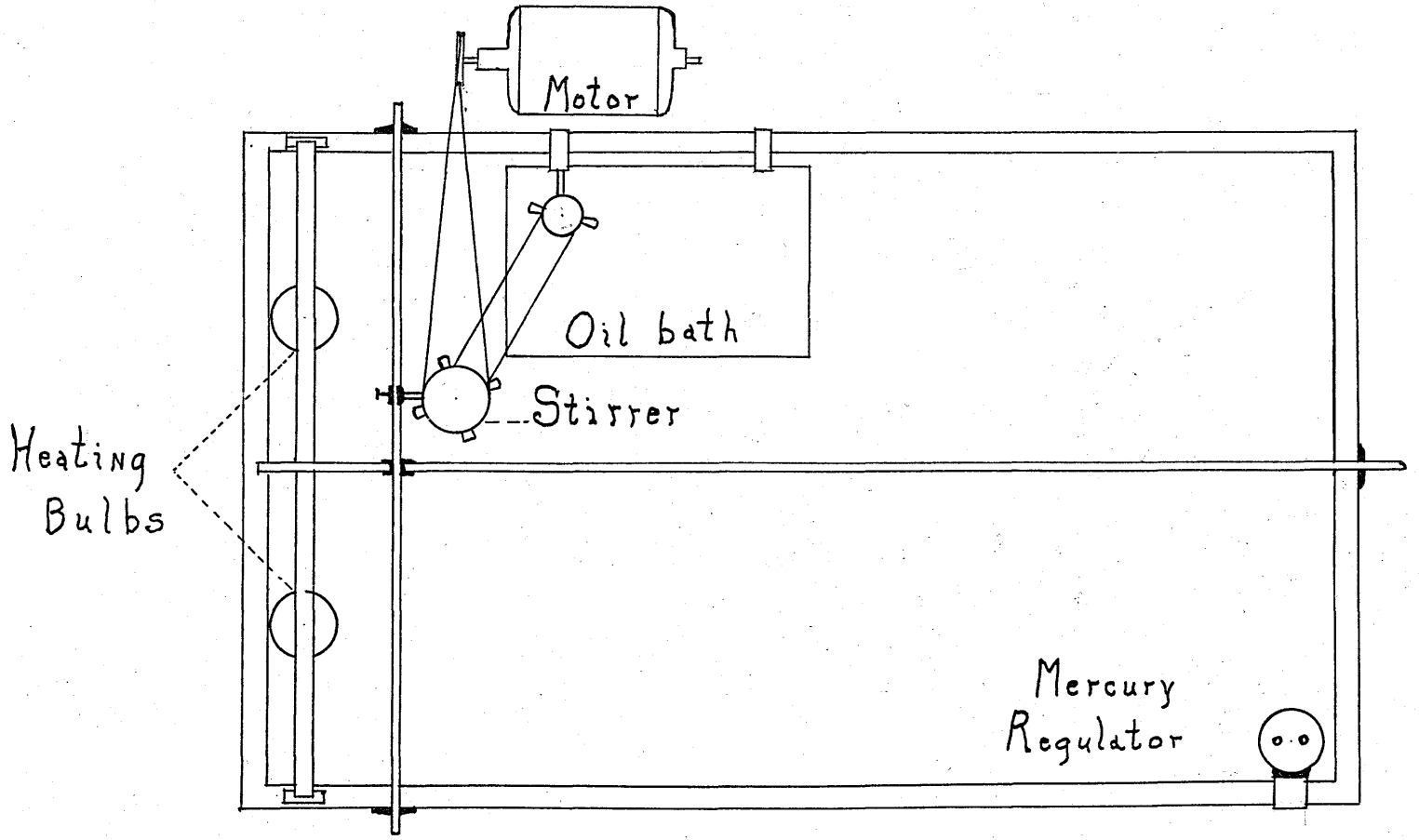
Cleaning the cells. The cells that were found defective in any were cleaned by first boiling them in hot water to remove the paint, and then allowed to stand over night in chromic acid cleaning mixture. According to Wolff and Waters (13) if the cells are left longer in the cleaning solution there is danger of forming lead chromate within the walls which is impossible to remove. The cells were next washed repeatedly in distilled water, dried in an oven at 110°, and corked until used again.

Introduction of Amalgam.- The amalgams were kept in weighing bottles and melted by placing in a water bath for the cadmium and in a parafine bath for the zinc amalgam. A quantity of the melted amalgam sufficient to fill the cell to at least 5 mm. was transferred to the cell by means of a heated, clean, dry pipette. The pipette was a straight piece of glass tubing, fire polished until the end was slightly smaller than the tube. A pipette drawn out to a capilliary would clog due to the cooling of the amalgam. After heating the pipette it was introduced below the surface of the amalgam and a gentle suction applied, the amalgam was prevented from running out by quickly closing the tube with the finger. Particles of the amalgam adhering to the tube were wiped off with a clean towel or filter paper, and the pipette introduced within 2 cm. of the bottom. The suction was released until the right amount of amalgam was in the cell, then applied and the pipette removed without touching the walls of the cell. Any amalgam adhering to the cell was removed with a glass rod. Before the amalgam had cooled the glass tube containing the platinum wire was placed in position and held in position with a glass rod while the crystals were being introduced. A cork notched for the passage of air was placed around the tube which held it permanently in position.

Introduction of crystals and solution.- Crystals were added to both sides to maintain concentration equilibrium at all temperatures. A saturated solution of salt was added by

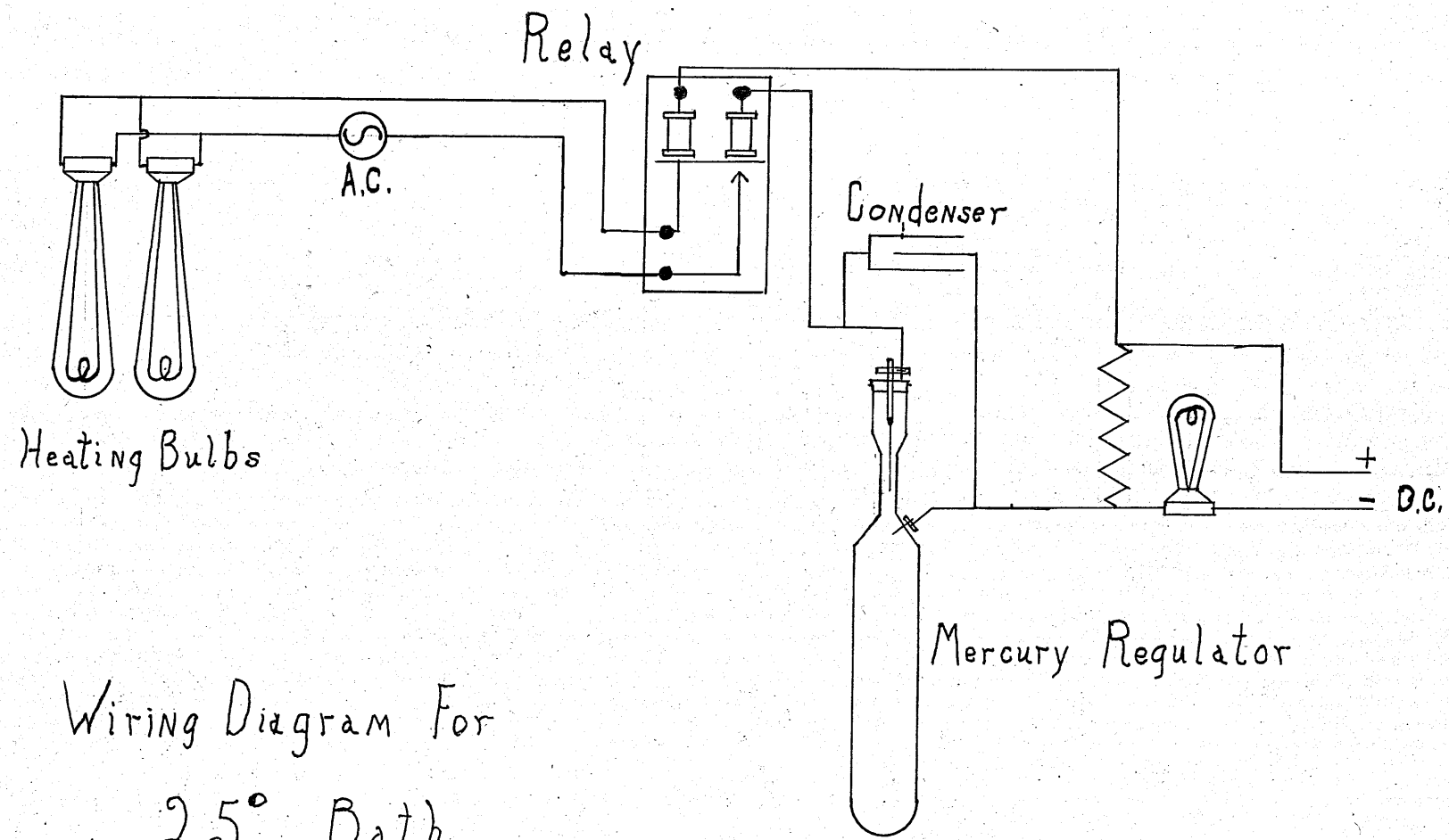
means of a clean and dry pipette to a height just a little above the cross arm.

The silver halide electrode prepared above was placed in position in the other limb of the cell. The Amalgamated copper wire was introduced on the amalgam side and each limb filled with enough sealing wax to make the copper wires solid, but leaving enough space for the cement. A stiff paste of litharge and glycerine was made and tamped in the remaining portion of the cell. If this cement is made from pure anhydrous glycerine the paste will take some time to set, but if a small amount of water is added it will set in a few minutes. After the cement had set the cells were dipped in black auto enamel, and set aside to dry. After they were dry they were placed in the 25° temperature bath for at least 12 hours before any measurements were made.



25° Temperature Bath

Figure III



Wiring Diagram For

25° Bath

Figure III

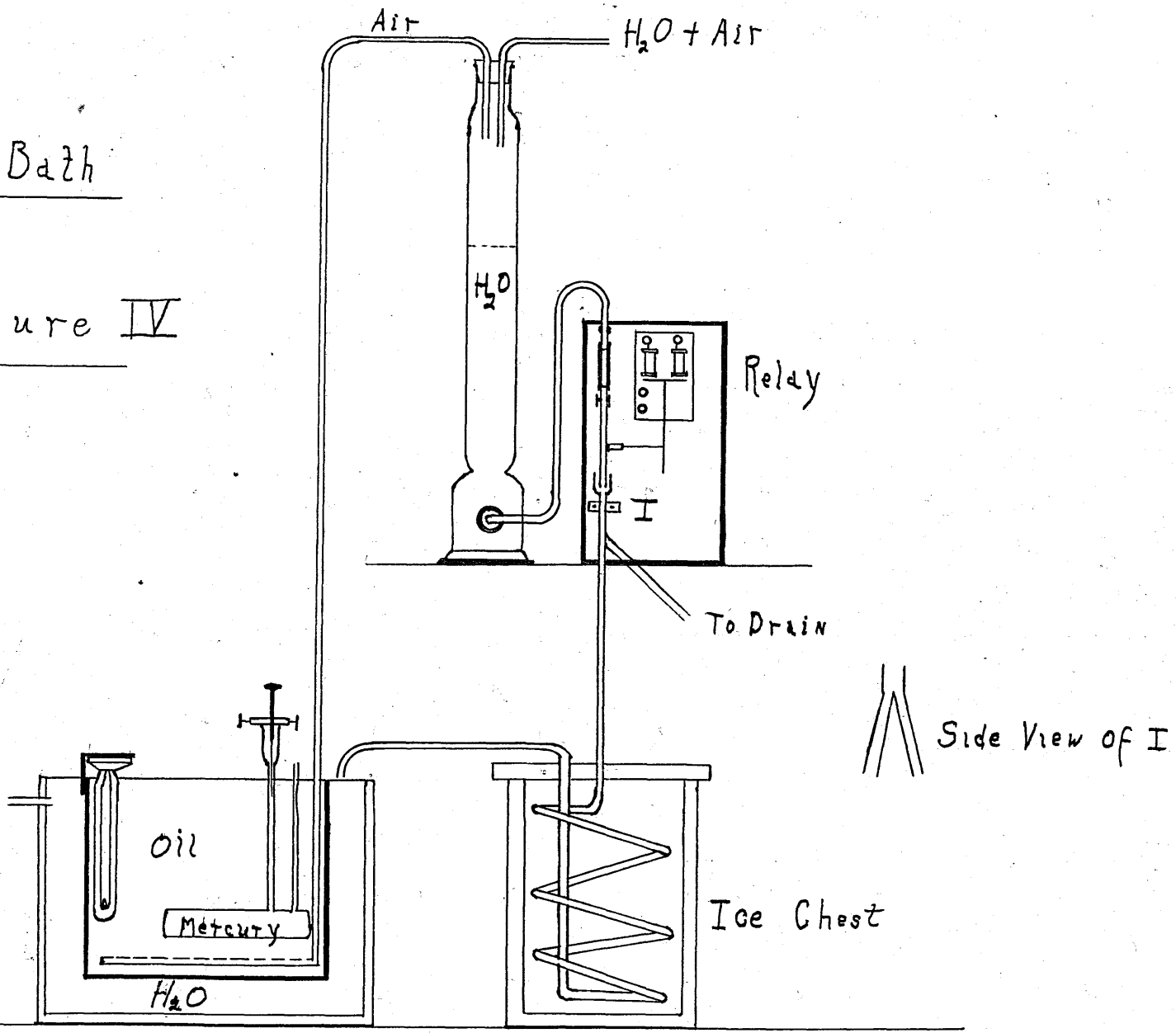
Temperature Baths.

25° Bath. This bath was of a type in regular use around the chemistry building, consisting of a porcelain tub 100 by 55 cm. and 50 cm. deep encased in an insulated wooden box. The temperature being controlled by a mercury bulb which made and broke the circuit to a 50-ohm relay which in turn made and broke the circuit to the heating bulbs. Heating bulbs have been found more efficient for constant temperature baths as they heat up and cool off more quickly than heating coils. Stirring was effected by means of a motor driven propeller forcing the water upward. A container for the cells consists of a glass rectangular dish filled with kerosene which was also stirred to prevent uneven heating effects. The large bath was filled with water. The temperature was regulated within 0.02° in the large bath but the temperature in the kerosene bath remained much more constant as it is not directly connected to the heating apparatus, and would not heat up or cool off as rapidly. Alternating current is used to heat the bath as it relieves the possibility of any direct current effects in measuring the potential of the cells. The current is supplied to the relay from the 110 D.C. as shown in figure 3.

15° Bath. A bath for measuring the potential of the cells at 15° was needed so that the temperature coefficients of the cells might be determined. This bath was designed as in figure 4 to work using tap water as the cooling source but as

15° Bath

Figure IV



Wiring Diagram For 15° Bath

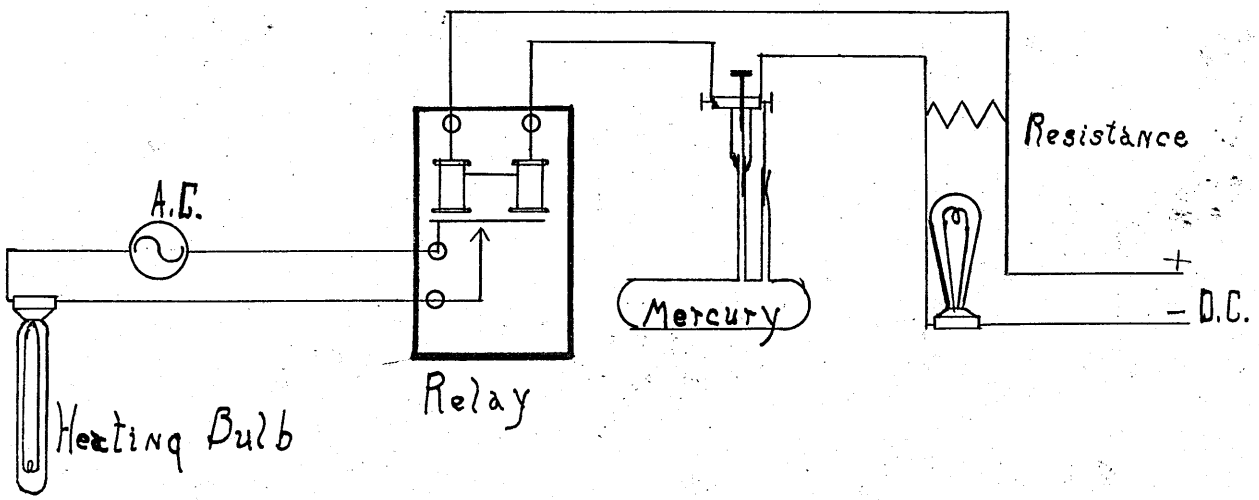


Figure V

the weather warmed an ice chest was constructed and the water going to the bath cooled by running it through a coil of lead pipe placed inside the ice chest. The outside container for the cold water is insulated with thick pasteboard and was made from a five gallon tin can; it is 24 cm. square and 18 cm. deep. The inside container is 20 cm. square and 15 cm. deep; this contains the heating bulb and mercury regulator. Tap water from an aspirator is brought to the top of the tower where the air separates and is used to stir the kerosene in the inside bath. The water in the outside container was not stirred, the current set up by the water entering and leaving stirred it enough, the temperature around the bath varying not more than 0.1°. The water from the tower goes to a short piece of metal tubing, which is connected to a longer pipe with rubber tubing, the longer pipe being parallel to the board on which it is fastened so that it is free to swing in a plane perpendicular to the board. The magnitude of the swing is controlled by the relay such that it swings directly over two pipes placed side by side. One of these pipes leads to the drain, the other to the lead coil. When the bath is too warm the mercury in the mercury regulator makes connection with a platinum wire closing the circuit to the relay, which breaks the circuit to the heating bulb and moves the pipe over the opening of the pipe that supplies water to outside container. The stream of water was so regulated that the temperature of the outside water was

around 13 degrees. When the bath is too cold the circuit to the relay is broken, the heating bulb is lighted and the water turned into the pipe leading to the drain. This arrangement gave the bath a very constant temperature, no change could be noticed in the position of the mercury in the thermometer.

Diagram of Connections For Measurments

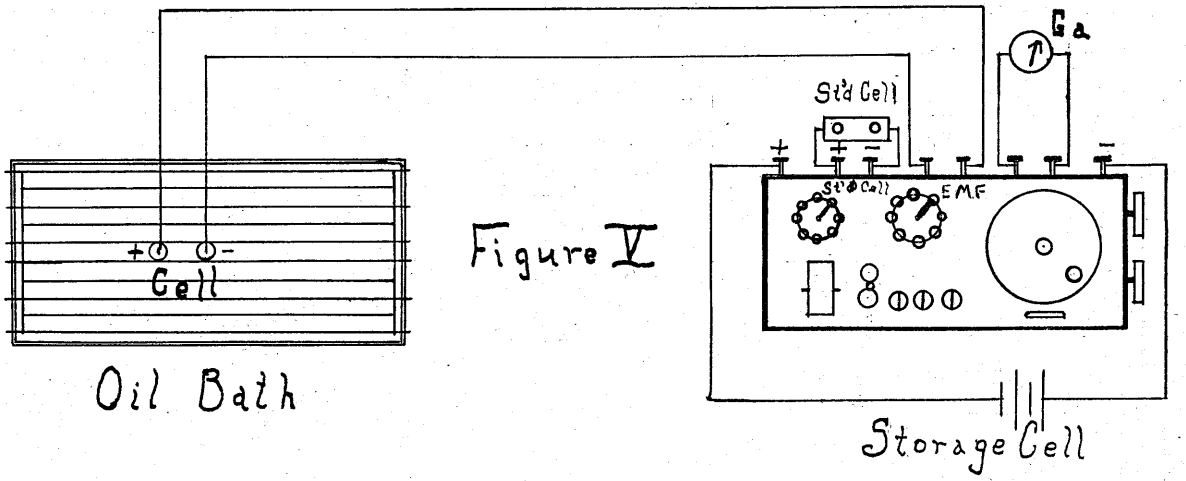
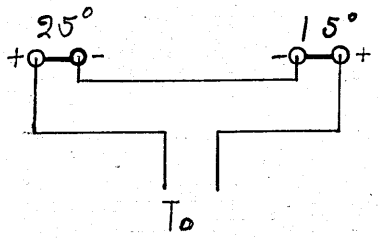


Figure V



Potentiometer

Figure VI

The electrical measurements.

Connections for the measurements are shown in figure V. All of the measurements were made with a Leeds and Northup type K potentiometer accurate to the fifth place. The potentiometer current was furnished by two cells of an Edison storage cell with extra resistance in the circuit. A high sensibility D'Arsonval galvanometer was used, made by the Willyoung Manufacturing company. A difference of 10 microvolts produced a deflection of 0.5 mm.

The standard cell was of the Weston type and was checked with two new Weston cells received from the Weston Instrument Company December 24, 1925.

Data on check.

No. Weston Cell	E.M.F.	Check on cell
5912	1.01874	1.01825
5912	1.01875	1.01823

The thermometers were graduated in tenths of a degree and checked with thermometers standardized by the Bureau of Standards.

Differences of potential between 25 degrees and 15 degrees was measured directly placing one cell at 25 degrees in series with the one at 15 degrees so that the potentials were against each other. The hook up is shown in figure VI.

Experimental.

When cells were made which checked within 0.1 millavolts one was placed in the 15° bath. Salts which crystallized out uniformily and were well defined in the literature were not analyzed, unless they failed to give reproducible cells.

I. Cd Amg : $CdCl_2$: $2.5H_2O$: AgCl : Ag. These were the first cells studied and the first ones were not reproducible, due in a large majority of cases to imperfect sealing, letting kerosene into the cell which caused it to gradually rise in potential. The first measurements were made at 25 degrees. In some of the first cells marked (#) crystals were not added and they were made up saturated at room temperature, about 20 degrees.

Table I

Date	number of cell					
1/11	1	2	3	4	5#	6#
1/11	.6222	.6390	.----	.6292		
1/22	.6242	.6392	.6236	.6225		
1/25	.6239	.6394	.6238	.6245		
2/2	.6320	.6305	.----	.6370		
2/4	.6333	.----	.6316	.6393		
2/6	.----	.----	.6292	.6270		
2/10	.----	.----	.63195	.6331	5#	6#
2/11	.----	.----	.6319	.63265	.6388	.63875

Table I (cont.)

Date	number of cell					
	1	2	3	4	5#	6#
2/12	.----	.----	.6320	.63266	.6391	.6389
2/13	.----	.----	.----	.----	.6391	.6389
2/15	.----	.----	.6331	.6325		
2/16	.----	.----	.6332	.6325		

	5#	6#	7	8
2/15	.63925	.63965	.----	.----
2/16	.63908	.6389	.----	.----

New(AgCl:Ag) electrodes were placed in all the cells.

	1	2	3	4
2/18	.6316	.6352	.6310	.63875
2/19	.6318	.63565	.6306	.63880
2/20	.6318	.63585	.6362	.6392
2/22	.6313	.63565	.63655	.63900
2/24	.6319	.63554	.63635	.6386
2/26	.6330	.63600	.63712	.63924

	5#	6#	7	8
2/18	.63518	.----	.----	.----
2/19	.63575	.----	.----	.----
2/20	.6360	.62717	.6242	.----
2/22	.6352	.62640	.6249	.63012
2/24	.63544	.62604	.62456	.63085
2/26	.63635	.62684	.62524	.63176

These cells were taken apart and new ones set up sealed with sealing wax and litharge cement. 5 and 6 were the only ones of this set which did not contain crystals.

Table I (cont.)

Date	9##	10#	11#	12#
2/26	.62708	.62510	.63165	.62452
3/1	.62737	.62517	.63175	.62490
3/2	.62787	.62509	.63175	.62554
3/5	.62791	.62515	.63185	.62563
3/11	.62791	.62557	.63189	.62569
3/16	.62815	.62460	.63105	.62500
3/17	.62853	.62482	.63145	.62528
3/20	.62931	.62518	.63173	.62555

	13	14	15##	16##
2/26	.62375	.----	.-----	.----
3/1	.62392	.----	.-----	.----
3/2	.62437	.62375	.-----	.----
3/5	.62445	.62385	.-----	.----
3/11	.62495	.62410	.-----	.----
3/16	.62400	.62370	.62615	.62461
3/17	.62423	.62393	.62648	.62482
3/20	.62448	.62420	.62660	.62851

Table I (cont.)

Date	9	10	11	12	13	14	15	16
3/23	.6297	.62530	.6320	.6256	.6246	.6244	.62915	.62925
3/25	.62945	.62529	.6320	.62555	.6245	.62438	.62855	.62930
3/27	.62925	.62529	.63205	.6256	.62463	.62438	.62866	.62934
3/30	.62890	.62524	.63210	.625625	.62460	.62440	.62884	.62929
4/5	.62967	.62528	.63200	,62562	.----	.62438	.----	.62931
4/10	.62867	.62527	.63200	.62562	.----	.62439	.----	.62930
4/15	.62845	.62528	.63206	.62562	.----	.----	.----	.62950
4/21	.----	.62518	.63178	.62500	.----	.----	.----	.----
4/24	.----	.62529	.63916	.62555	.----	.----	.----	.----
4/26	.----	.62523	.63184	.62545	.----	.----	.----	.----
5/1	.----	.62520	.63176	.62549	,----	.----	.----	.----

	17	18	17 at 15°	Difference between 17 & 18 at 15° measured.
3/29	.6240	.6239		
4/5	.6241	.6240		
4/10	.62395	.62395		
4/15	.62384	.62384		
4/16	.----	.63245		
4/17	.----	.62367	.62768	.00402
4/19	.----	.62410	.62810	.00400
4/21	.----	.62400	.62800	.00400

Explanation of Table I

Cells number 9, 15, 16 were made with different style silver chloride electrodes marked ## prepared as by Linhart (14). Finely divided silver was mixed with powdered silver chloride and tamped around a silver spral at the bottom of the cell, connections being made as before. The Ag was prepared by electrolytic deposition using a current of 5 to 7 amperes having a platinum wire as the cathode and pure silver as anode in a silver nitrate solution. The silver appeared in spongy clots which were removed and washed with distilled water. The AgCl was precipitated from silver nitrate solution with HCl. The silver and silver chloride mixture was washed with cadmium chloride solution before putting in the cell. These were abandoned because they were more difficult to set up and were not as constant as the others.

Cells number 10, 11, and 12 were made from a saturated solution of cadmium chloride at 20° without crystals. The others were made as usual. The date of setting up was three days before the first reading.

Calculation of Heat of Reaction

The values for the potential between cadmium and cadmium amalgam was taken from data collected by Hulett (15).

Potential of Cd:Cd Amg $25^{\circ} = 0.05053$

$18.2^{\circ} = 0.05225$

$0^{\circ} = 0.05663$

$15^{\circ} = 0.05302$ (Calc.)

E.M. F. of Cell / E.M.F. of (Cd:Cd Amg.)

Date	No.		dE/dT
	17 15^{o}	18 25^{o}	
4/17 (1)	.62768/.05302=.68070	.62367/.05053=.67420	00065
4/19 (2)	.62910/.05302=.68112	.62410/.05053=.67463	000649

From Gibbs-Helmholtz Equation.

Q = heat of reaction of the salts

N = Number of moles in a molecule of the salt in solution

dE = Change in E.M.F. due to temperature

dT = Change in temperature

F = 96,496 coulombs or I farady

T = (273 / t)

(1) Q = 2 X 96,496 (.6742 / 298 X .00065) = 167,497.7 joules

= 40,040 calories

(2) Q = 40,041 calories

4.183 joules = 1 calorie

The equation for the heat of reaction is,

$Cd + 2AgCl + 2.5H_2O = CdCl_2 2.5H_2O + 2Ag$

Thomsen (16) gives for the heat of formation of $CdCl_2 2.5H_2O$ (98,530 calories) and for AgCl (29,380 calories).

Taylor (1) determined the heat of reaction using the same cell as (40,030 calories)

The thermo chemical data gives for Q (39,770 calories).

The values determined chemically check as well as can be expected with the thermo-chemical data.

II. Cd Amg : $CdCl_2.NH_4Cl$: AgCl : Ag

$CdNH_4Cl_3$ was prepared according to Baxter and Hines (17). Equi-molar proportions of the two salts were brought into solution and the solution concentrated until the salts began to crystallize out. The crystals were well defined needles very soluble in hot water. The crystals were dried by suction and a saturated solution was made in distilled water in contact with crystals of the salt.

	Cells No. 25°		15°	Measured potential between
Date	19	20	19	19 & 20
3/30	.65374	.65357		
4/5	.65355	.65355		
4/10	.65345	.65345		
4/15	.-----	.65338	.65010	.00350
4/17	.-----	.65356	.65012	.00332
4/19	.-----	.65380	.65070	.00300
4/21	.-----	.65380	.65105	.00272
4/24	.-----	.65317	.65317	

Difference of potential between Cadmium and cadmium amalgam

at 15° to 25° = .00249 0.0003 + 0.00249 = 0.00549 = dE

dE/dt = .000347

Q = 2 X 96,496 (.70443 - 298 X .000549) = 104,299 joules

= 24,934 calories

III.

Cd Amg : $CdCl_2.KCl.H_2O$: AgCl : Ag

$CdKCl_3.H_2O$ was prepared according to H. Croft (18); equi molar portions of the two solutions were brought into solution and evaporated until crystallization began. The salt formed definite crystals and a solution made as before.

Date	Number of cell				
	21 At 25°	22	23	15° 21	Measured difference between 21 & 22
2/26	.65800				
3/11	.65810				
3/20	.65801				
3/25	.65806				
3/20	.65906	.65906	.65815		
4/5	.65805	.65822	.65740		
4/10	.65800	.65814	.65735		
4/15	.65805	.65810	.65730		
4/19	.----	.65811	.65740	.65887	.00073
4/21	.----	.65810	.65725	.65880	.00071
4/24	.----	.----	.65725		
4/26	.----	.65813	.65730		

$dE/dT = -.000321$

$Q = 34,799$ calories

IV.

$ZnCl_2 2NH_4Cl.H_2O$ was prepared by bringing into solution one mole of zinc chloride and one of ammonium chloride and evaporating the solution until crystallization began. The crystals were well formed plates and according to Base (19) contain one mole of water. The crystals were dried by suction, and a saturated solution made with distilled water.

Zn Amg : $ZnCl_2.2NH_4Cl.H_2O$: AgCl : Ag

Date	Number of cell						
	24	25 at 25°	26	27	28	29	25 at 15°
3/23	.93160	.93183	.96245	.9620			
3/25	.93160	.93184	.96115	.96157			
3/27	.93233	.93173	.96075	.96120	.96174	.96120	
4/5	.93190	.93162	.96050	.----	.96150	.96056	
4/10	.93192	.93153	.96045	.----	.96135	.95795	
4/15	.93130	.93130	.95960	.----	.96126	.95775	
4/17	.93120	.----	.95950	.----	.----	.----	.93602
4/19	.93145	.----	.----	.----	.----	.----	.93635
4/21	.93147	.----	.----	.----	.----	.-----	

The average of the potential differences measured was -.00502 then $dE/dT = -0.000502$

$Q = 49,900$ calories

The first two cells were made from the first crop of crystals from the solution and were uniform. The others were made from the second crop which were not so well formed, and probably contained crystals of the mono derivative.

V.

Zn Amg : $ZnCl_2.2KCl.H_2O$: AgCl : Ag

$ZnK_2Cl_4.H_2O$ according to Ephraim (20) this salt is formed whenever a mixture of these two salts are brought in solution. A mixture of one mole of zinc chloride and two moles of potassium chloride was brought into solution and evaporated to crystallization. The crystals were small and not well formed but they were redissolved in distilled water and some cells made which were not reproducible, so the solution was recrystallized but still the cells were not reproducible. A new mixture was brought into solution and the first crop of crystals discarded. The second and third crops from this mother liquor gave well formed crystals which were analyzed and found to be the desired salt. The zinc was determined by the ferrocyanide method. A solution of $K_4Fe(Cn)_6$ was standardized against pure zinc, 1 cc. = 0.0048 gr. Zn.

Weight Zinc	S_1 .1812	S_2 .1831
CC. of $K_4Fe(Cn)_6$	37.8	38.2
Gram of zinc/cc	.00479	.0048

Some crystals from the second crop were dried in an oven for 4 hours at 35° and analyzed, some crystals from the third crop were dried at 100° for 3 hours. The salt loses its water of crystallization at 90° so the anhydrous salt was expected from the dried third crop.

	Analysis of 2nd		of 3rd dried	
Weight of salt	S_1	S_2	S_3	S_4
	1.2104	0.6507	0.4917	0.6525
Cc. of $K_4Fe(Cn)_6$	55	30	23.5	30.9
Percent of zinc	21.8	21.53	22.9	22.75
Theoretical %	21.52		22.9	

Zn Amg : $ZnCl_2.2KCl.H_2O$: AgCl : Ag

Date	Number of cell						
	29	30	31	32	33	34	35
3/23	.89645	.94530					
			Recrystallized				
3/25	.89644	.94543	.96300				
				Salt			
3/27	.89660	.94550	.9660				
3/30	.89667	.94567	.96686				
4/5	.89660	.94596	.96690	1.04109			
4/10	.89660	.94580	.9670	1.0407			
4/15	.89640	.94584	.96630	1.04075			
4/19			.96740	1.04072	.96890		
4/21			.96719		.9690		
4/26					.96935		
5/1					.96950		

Cells made up from the analyzed salt were very satisfactory. As $ZnK_2Cl_4H_2O$ is formed whenever the two salts are brought into solution some cells were tried which were saturated with KCl as well as the double salt. Crystals of the double salt were studied under the microscope. The crystals of the anhydrous double salt are long rectangular thin lath-like plates. The crystals with one mole of water are rhombic either long or uniform hexogal shape.

Cells from analyzed salt

	34	35	34 15°	Measured difference between 34 & 35, 0.0014
5/1	.96795	.96815		
5/3	.-----	.96719	.96678	

$dE/dT = 0.000139$

$Q = 40,665$ Calories $\quad E_o = .968000$

Cells saturated with KCl and $ZnK_2Cl_4 \cdot H_2O$

	36	37	36 15°	Measured difference
5/1	.96854	.96848		
5/3	.-----	.96850	.96870	.00021
5/4	.-----	.96850	.96855	.00005
5/6	.-----	.96830	.96835	.00005
5/7	.-----	.96800	.96795	.00005
5/12	.-----	.96810		
5/13	.-----	.96800		

$dE/dT = .000005$

$Q = 44,662$ Calories $\quad E_o = .96800$

	38	39	40	38 - 15°
5/10	.96832	.-----		
5/10	.96782	.-----		
5/12	.96820	.96745	.96850	
5/13	.-----	.96763	.96840	.96830

AgBr : Ag electrodes.- The silver bromide electrodes prepared as above which checked among themselves failed to give satisfactory reproducible cells. More electrodes were prepared using a smaller current (0.15 amperes). This gave electrodes which checked but it was difficult to form an even coating around the silver bromide cylinder. Cells made from these also failed to check. A study was then made of the best means of forming the electrodes. A 10% solution of ammonium bromide was used as the electrolyte, when running the electrodes alternately as anode and cathode. This gave a gray silver deposit, instead of a black one as was the case when hydrobromic acid or a solution of potassium bromide was used. The silver was also more adherent to the silver bromide cylinder and would not pile up in a bunch as the black deposit would if the electrode was reduced for a long time. Using this small current the time between each alternation was changed to thirty seconds. Using the NH_4Br solution only one satisfactory even coated electrode was prepared out of a dozen trials. No electrolytic method for forming the electrodes has as yet been perfected that will give a reproducible cell every time. Electrodes which had not been run electrolytic were tested with the potentiometer and found to check within 0.00025 volt of each other, so cells were set up with these and were fairly reproducible.

Cells saturated with double salts are not entirely reversible as either cadmium or zinc is going into solution forming an excess of their respective salt. This leads to a study of solutions of the salts which were saturated with either potassium bromide or ammonium bromide and the double salt. The composition of the double salt was changed in some cases to the stable one in an excess of the potassium or ammonium bromide. The salts were all prepared in the same way. A saturated solution of either zinc or cadmium bromide was saturated with either potassium or ammonium bromide and the mixture raised to the boiling point. If the solution was not saturated at the higher temperature with the alkali salt more was added. The solutions were set aside to crystallize and the crystals afterwards studied with a microscope, when only two forms of crystals could be detected one corresponding to the double salt and the other to either potassium or ammonium bromide; it was evident that the double salt contained the largest number of moles of potassium or ammonium bromide that was possible in contact with an excess of that salt.

$CdBr_2.4H_2O$.- This salt prepared as above crystallized out in long needles. A saturated solution was made using an excess of the crystals and cells made from it. The cells did not check due to the electrodes as described above.

Cells with Electrodes Prepared in KBr

Date	No of cell		all at 25 degrees		
	41	42	43	44	45
3/6	.49150				
3/20	.49195				
3/27	.49745				
4/5	.49690	.48704	.48760		
4/10	.49691	.48736	.48770		
4/15	.49620	.48740	.48045		
4/19	.-----	.48865	.49050	.48615	.48460
4/21				.48519	.48450
4/24				.48510	.48400
4/26				.48524	.48413

Electrodes Prepared in HBr

5.1				Defective	.48570

Electrodes not Electrolytically Treated

5/1	46	47	46 at 15 degrees	
5/1	.4864	.48439		
5/10	.4864	deff.		
5/12	.48646			
5/13	6 hours later		.49310	
	12 hours later		.49310	difference 0.00664

dE/dT for Cd : Cd Amg = -0.000249

De/Dt for cell = -0.000913

Q = 37,634 calories

Thomsen's Thermo chemical data gives

Q = 37,530 calories

$CdBr_2NH_4Br$.- This salt was made from a solution of the two salts in proportion of (1:1). The solution was concentrated until the salts began to crystallize out. The crystals were dried by suction and were long needles. The cells were made up from a solution of the double salt saturated with crystals. References H Croft (18), Ephraim (20).

Electrodes run in KBr

Number of cell - all at 25°

Date	48	49	50
4/5	.47735	.47935	
4/10	.47699	.47895	
4/15	.47645	.47900	
4/19	.47670	.47907	.48950
4/21	.-----	.-----	.47810

Electrodes in HBr 25°

	51	52
4/26	.47693	.49420
5/1	.48037	.48430
5/3	.48245	.48150
5/5	.48280	.48100

Electrodes not treated electrolytically

These cells were made from salts that were saturated with NH_4Br forming the double salt $CdBr_2 4NH_4Br$ which is stable in an excess of NH_4Br. The cells were made saturated with crystals of the double salt and NH_4Br. The crystals according to Rimbach are triognal and double refracting; this was

confirmed by studying the crystals with a microscope.

Cd Amg : $CdBr_2 4NH_4Br(NH_4Br)_x$ - AgBr : Ag

Date	Number of cell at 25° 53	54	54 - 15°	Measured difference 53 & 54
5/10	.55324	.55301		
5/12	.55340	.55290		
5/13	.55355	.55260		
6 hr. later	.55355	.-----	.54920	.00410
12 hr. later	.55355	.-----	.54930	.00400

Difference between 53 and 54 = .00095

Difference between 54-25° and

54-15° = .00040

= .00330

Difference calculated from

measured difference

.00410 - .00095 = .00315

.00400 - .00095 = .00305

mean = 0.00325

dE/dT for Cd : Cd Amg = 0.000249

0.000325

dE/dT for cell = 0.000574

E_{25} = .55307 + .05053 = .60360

$$Q = \frac{2 \times 96{,}496(.6036 - 298 \times .000574)^2}{4.183}$$

Q = 19,496 Calories

$CdBr_2KBrH_2O$.- This salt was prepared the same as the NH_4Br derivative. Using proportions of 1:1 giving a double salt crystallizing out in needles with one mole of water of crystallization according to K. Von Hauer (22). (The cells were made from a saturated solution with an excess of the crystals.)

Electrodes prepared in KBr

Date	Number of cell at 25°		
	55	56	57
4/5	.48846	.49240	
4/10	.48841	.49136	
4.15	.49105	.49172	
4/19	.49090	.49145	.49065
4/26	Deff.	.49235	.48832
5/4	.----	.49238	Defective
5/6	.----	.49240	.e---
5/12	.----	.49255	.----

Electrodes prepared in HBr

	58	59	59-15°	
4/26	.49390	.49490		
5/1	.49270	.49101		
5/3	.49300	.49100		
5/5	.49330	.49100		difference
5/12	Def.	.49040		
5/13		.-----	.49290	.00250
6 Hr. later		.-----	.49292	.00252

$$dE/dT = .000251 \neq .000249 = .0005$$

$$E_{25} = .49188 \neq .05053 = 0.54241$$

$$Q = \frac{2 \times 96,496}{4.183}(0.54241 - 298 \times 0.0005) = 18,151 \text{ Calories}$$

Electrodes not prepared electrolytically

These cells besides using a different electrode were filled with a saturated solution of the double salt which was saturated with KBr, also with crystals of the double salt and of KBr. The crystals of the double salt ($CdBr_2 4KBr$) formed under these conditions according to K. Von Hauer (22) are isomorphous with the crystals of the corresponding chlorine compound, which are rhombohedral (ditrigonal). Under the microscope they appeared as long needles. The cells made from this salt showed that the double salt had a probable composition of $CdBr_2 4KBr$.

	Cd Amg : Cd $Br_2 4KBr(KBr)_x$: AgCl : Ag	
Date	60 - 25°	61
5/10	.56210	.56100
5/12	.56205	.56480
5/13	Def.	.56665

$ZnBr_2 2HN_4BrH_2O$.- This salt is prepared according to Rammelsberg (23) using the proportions 1:2; this gave a salt which hydrolyzed in water but the first cells were made from it. According to Jones and Knight (24) a mixture to the di and tri ammonium bromide salts are formed. $ZnBr_2 3KBrH_2O$ was prepared using proportions 1:3 the first crop of crystals was almost all NH_4Br containing less than 1 percent of zinc by analysis. The mother liquor gave crystals which when analyzed for zinc gave the right percentage for the composition $ZnBr_2 3NH_4Br.H_2O$, using the ferrocyanide method.

			2nd crop from liquor	
Wt. of sample	S_1	S_2	S_3	S_4
	.8816	1.2553	1.0916	1.1191
cc. of $K_4Fe(CN)_6$	23.6	33.3	29.9	30.5

1 cc. of $K_4Fe(CN)_6$ = 0.0048 gram of zinc.

percent of Zn	12.85	12.96	13.1	13.07

Theoretical percent of zinc = 13.05

	Electrodes prepared in KBr			
Date	62	63	64	65
4/10	.77163	.76887		
4/15	.77310	.76982		
4/19	.-----	.-----	.81230	.82500
4/21			.80022	.81775
4.24			.78590	.80864
4/26			.78438	.80580
5/1			.78920	def.

Electrodes prepared in HBr

Date	66	67
4/20	.81006	.80730
4/26	.81300	.80443
5/1	.81350	Def.

$ZnBr_2 3NH_4Br.H_2O$.- This salt was kept from hydrolyzing by saturating the solution with NH_4Br. The electrodes were not prepared electrolytically.

Zn Amg : $ZnBr_2 3NH_4Br.H_2O(NH_4Br)_x$: AgBr : Ag

Date	Cell at 25°			
	66	67	66-15°	measured difference
5/10	.78740	.79800		
5/12	.78580	.78640		
5/13	.78650	.78751		$\frac{66-67}{15°-25°}$
6 hr. later	.78678	.78722		
12 hr. later	-----	.78742	.78910	-.00150

Calculated difference for 66 at 15° to 25°

from measured value = -0.00214

$dE/dT = 0.000214$

$$Q = \frac{2 \times 96,496}{4.183}(0.78700 + 298 \times 0.000214)$$

$Q = 39,298$ Calories

$ZnBr_2 2KBr.2H_2O$.- Was prepared according to Ephraim (20) using proportions 1:2; the salt is easily prepared forming well defined crystals. The crystals are isomorphus with the corresponding chlorine compound and are formed no matter what proportions are used. The crystals studied under a microscope were the same as those of the potassium chloride derivative. A satisfactory cell was made from the first using the electrodes prepared with KBr. The electrodes prepared without any solution were not constant for this cell.

An Amg : $ZnBr_2 2KBr.2H_2O$: AgBr : Ag

Cells at 25°

Date	68	69	68-15°	Measured difference between 68-69
4/10	.82234	.82238		
4/15	.-----	.82239	.81904	.00342
4/16	.-----	.82245	.81725	.00485
4/19	.-----	.82252	.81800	.00455
4/26	.-----	.82140		

dE/dT = 0.00047

Q = 31,482 calories

Cells with dipped electrodes and saturated with KBr

	70	71
5/10	.73865	.81100
5/12	.74365	.80050
5/13	.74495	.79300

Conclusions

At the present stage of experimentation the chloride cells are much more reproducible than the bromide cells. This is probably due to the bromide electrodes, as a method for their preparation was not developed which gave a satisfactory electrode every time.

Of all the cells studied the cell of the type

Zn Amg : $ZnCl_2 2KCl.H_2O(KCl)_x$: AgCl : Ag

gave the most promise of a satisfactory standard cell, having a possible E.M.F. of 0.96800 and a negligible temperature coefficient.

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